



The impact of urea on the performance of metal exchanged zeolites for the selective catalytic reduction of NO_x

Part I. Pyrolysis and hydrolysis of urea over zeolite catalysts

Maik Eichelbaum^{a,*}, Robert J. Farrauto^{a,b}, Marco J. Castaldi^a

^a Department of Earth and Environmental Engineering (HKSM), Columbia University in the City of New York, 500 West 120th Street, New York, NY 10027, USA

^b BASF Catalysts LLC, 25 Middlesex Turnpike, Iselin, NJ 08830, USA

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ABSTRACT

Urea-SCR over metal exchanged zeolites is one of the leading catalytic technologies to abate NO_x emissions in diesel exhaust. Ideally, urea injected into the diesel exhaust upstream of the SCR catalyst decomposes only to the gaseous products CO₂ and NH₃, where the latter gas can react with NO_x emissions to form harmless N₂ and H₂O. However, solid by-products can be formed as well, and if deposited on the catalyst harm the long-term catalytic performance. In order to identify the impact of various urea decomposition products on the catalytic activity, we studied the pyrolysis and hydrolysis of neat urea and of urea over different zeolites (H-Y, Cu-Y, H-Beta, Na-Beta, and Fe-Beta). The experiments were run in dry and steam-containing N₂ between 20 and 750 °C by using simultaneous thermogravimetric analysis (TGA), differential thermoanalysis (DTA), and online GC/MS evolved gas analysis. Solid intermediate products at different decomposition temperatures were identified by means of ATR-FTIR and luminescence spectroscopy. As for neat urea, CO₂, NH₃ and HNCO could be detected as major gaseous products. At 270 °C significant amounts of cyanuric acid and ammelide and at 500 °C of melem and melon were identified as solid intermediates. Above 625 °C, all solid residues decomposed to cyanogen and isocyanic acid. Furthermore, it could be shown clearly that the investigated zeolites significantly accelerate the pyrolysis of urea and cyanuric acid, and the hydrolysis of HNCO, by shifting the decomposition processes to lower temperatures and by inhibiting the formation of solid by-products. In addition, the presence of steam in the feed gas can prevent even further the formation of solid residues and the high temperature adsorption of gaseous products.

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1. Introduction

Diesel engines are an attractive alternative to gasoline internal combustion engines because they operate with high compression ratios and lean air–fuel mixtures making them 20–40% more fuel efficient. However, due to the large amounts of excess air in the exhaust the gaseous, liquid, and solid emissions cannot be abated by simply using the three-way catalyst strategy of gasoline cars [1–3]. The simultaneous abatement of both nitrogen oxides (NO_x) and particulate matter is challenging, a problem that apparently cannot be solved by improved engine management alone [3]. NO_x causes ground level ozone (smog), induces the formation of toxic

chemicals as well as acid rain, and it is therefore regulated in the U.S. by the Environmental Protection Agency (EPA). As NO_x standards are becoming more stringent for diesel motor vehicles under the EPA Tier 2 program as well as under EURO V and VI regulations in Europe, and since there is a trade-off between low NO_x emissions and low fuel consumption, the need for NO_x abatement technology is growing [1,2,4].

In power plants and stationary sources, selective catalytic reduction (SCR) by NH₃, which transforms NO_x into harmless N₂ and water vapor, has already proven itself for the successful reduction of NO_x emissions in flue gases [5,6]. Furthermore, the installation of a powerful catalytic NO_x abatement technology can reduce diesel fuel consumption by as much as 7% by allowing the engine to be optimized on fuel economy [4]. Thus, a successful implementation of SCR in diesel cars and trucks bears the potential for building vehicles that emit not only less NO_x, but generate significantly less of the greenhouse gas CO₂ as well.

Since NH₃ is a reactive and toxic gas it is proposed to use an aqueous urea solution containing 32.5% by weight (wt.%) urea (also

* Corresponding author. Present address: Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany. Tel.: +49 30 8413 4566; fax: +49 30 8413 4401.

E-mail address: me@fhi-berlin.mpg.de (M. Eichelbaum).

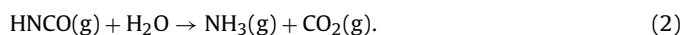
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referred to as AdBlue®) as the NH_3 source for SCR in transportation applications due to its non-toxicity and the ability to be carried on board much more easily and safely [3,4,7,8]. For stationary sources and originally also for mobile diesel applications vanadia-based catalysts have been used as NH_3 -SCR catalysts [5]. However, the low activity at low temperatures, the low selectivity at high temperatures, and the problems associated with the release of toxic vanadium during operation have triggered many research activities to find better urea-SCR catalysts for mobile diesel applications. Metal-exchanged zeolites such as copper- and iron-based ZSM-5 [3,9–11] show very high activities and selectivities towards urea-SCR over a broad temperature range. Fe-exchanged BEA zeolites have superior SCR activities even outperforming typical vanadia on anatase catalysts [12].

After the injection of urea solution into the hot diesel exhaust upstream of the catalyst water evaporates and urea decomposes first into equimolar amounts of gaseous NH_3 and isocyanic acid (HNCO) [8,13–16].



In a subsequent reaction HNCO has to react with water forming NH_3 and CO_2 [8,13–16].



However, reaction (2) is rather slow at typical diesel exhaust temperatures, and thus demands an additional hydrolysis catalyst. Fortunately, common oxide catalysts used for SCR can catalyze this reaction making a hydrolysis catalyst redundant [17–19].

However, it has been reported that solid components such as cyanuric acid (CyA), ammeline, ammelide or melamine can be formed during urea pyrolysis, too [13,14,16,20,21]. White or pale beige precipitates were even identified on SCR catalysts subsequent to engine or lab reactor tests with urea injection [14,22,23]. Furthermore, Cheng et al. and Xu et al. simulated the urea decomposition on SCR catalysts by spraying aqueous urea solution on monolithic Cu-exchanged zeolites followed by a hydrothermal treatment at temperatures above 700 °C and observed a diminished SCR activity [23,24]. The urea-induced deactivation of the catalyst was beyond that found by hydrothermal aging alone. The formation of unwanted by-products could not only decrease the amount of NH_3 formed by urea decomposition, but could also poison the SCR catalyst and thus could significantly decrease its lifetime. Heavy-duty diesel vehicles must fulfill the NO_x emission standards even after much more than 400,000 miles of driving. Consequently, even a slight negative impact of urea might seriously affect the catalytic performance after such long operation times. Hence, the detailed investigation of the urea decomposition on SCR catalysts is required to understand any possible catalyst deactivation mechanisms and to develop strategies preventing a negative influence of urea for the long-term performance of diesel SCR catalysts for optimum NO_x abatement. So far only the effect of vanadia-based catalysts on urea decomposition was studied [14], whereas the impact of zeolite-based SCR catalysts has to the best of our knowledge not been thoroughly investigated yet.

We studied the decomposition of neat urea and of urea/zeolite mixtures. The investigated zeolites were H-Y, Cu-Y, H-Beta, Na-Beta, and Fe-Beta. Urea decomposition was investigated by means of simultaneous thermogravimetric (TG) and differential thermoanalysis (DTA) in the temperature range between 20 and 750 °C in both dry and steam-containing N_2 . The gases evolved during the reactions were detected by online GC/MS. Solid intermediates of the decomposition at 270, 300, and 500 °C were characterized by attenuated total reflection (ATR) FTIR and luminescence spectroscopy. The impact of the deposits on the SCR performance of

metal exchanged zeolite catalysts is reported in part II of the companion paper [25].

2. Experimental

2.1. Sample preparation

32.5 wt.% aqueous urea solution for impregnation was prepared by dissolving the appropriate amount of urea (Fisher Scientific) in deionized (D.I.) water. The zeolites H-Y, Cu-Y, H-Beta, Na-Beta, and Fe-Beta were prepared by ion exchange of the NH_4 -forms of the appropriate zeolites. For impregnation with urea typically 1.0 g of the catalyst powder was wetted with the appropriate amount of 32.5 wt.% aqueous urea solution followed by drying the sample under ambient conditions. Alternatively, samples were prepared by mechanically mixing the catalyst with appropriate amounts of dry solid urea. Catalyst/cyanuric acid (98%, Acros Organics) mixtures were prepared in a similar way with the dry components being the starting materials.

2.2. Characterization techniques

Thermogravimetric and differential thermoanalysis in dry atmospheres was performed with a TG-DTA/DSC apparatus (Netzsch STA 409 PC Luxx) equipped with a TG/DTA sample carrier using corundum pans. As purge and protective gas dry N_2 (UHP grade) was used. The flow rate was set to 80 ml/min. TG experiments in humid atmospheres were done with the TG-DTA/DSC instrument Netzsch STA 449 F3 Jupiter with steam furnace equipped with a TG sample carrier and corundum sample pans. The desired amounts of steam were provided by a saturator operated at controlled temperatures. The steam concentration in the purge gas was monitored by means of an online dew point measurement (EdgeTech DewPrime I). The flow rate was controlled by mass flow controllers (Aalborg GCF17) and set to 200 ml/min. Alternatively, measurements were run in dry atmospheres with the same apparatus and equivalent flow rates, but by using the dry purge gas without saturating it with water. Both TG instruments could be connected to a GC/MS system (gas chromatograph Agilent 6890 series equipped with a fused silica column (Varian CP7447), and coupled to the mass selective detector Agilent 5973Network) by heated transfer lines to analyze evolved gases. For this purpose experiments were first run in scan MS mode to identify all gaseous decomposition products. The data shown were acquired by using the single ion mode (SIM) to monitor the mass/charge ratios 17 (NH_3), 18 (H_2O), 43 (HNCO), 44 (CO_2), and 52 ($(\text{CN})_2$) with highest sensitivity.

Solid decomposition products were characterized with a Bio-Rad FTS 6000 FTIR spectrometer equipped with a DuraSamplIR™ Diamond ATR (attenuated total reflection) unit.

Photoluminescence spectra of the urea residues were recorded at room temperature with the Ocean Optics HR2000 spectrometer equipped with a Schott KV370 long pass filter to suppress excitation light. Excitation was carried out with the pulsed N_2 -laser MNL 103-PD from Lasertechnik Berlin (wavelength: 337.1 nm, pulse energy: 80 μJ , repetition rate: 20 Hz, pulse duration: 3.5 ns).

3. Results and discussion

3.1. Pyrolysis of neat urea

In order to understand the impact of urea deposited on SCR catalysts it is necessary to study the decomposition under conditions as close to real conditions in the diesel exhaust stream as possible. Even though several studies regarding the pyrolysis of urea have been published [13–16,20,21], the influence of

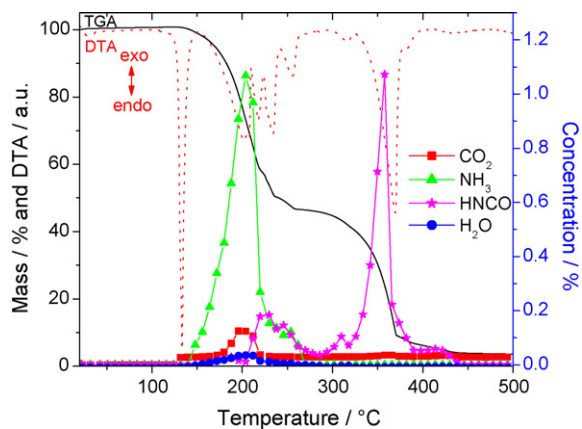


Fig. 1. TGA, DTA graphs and quantitative results of the GC/MS evolved gas analysis of the decomposition of neat urea in dry N_2 (initial weight: 60 mg; heating rate: 2 K/min; flow rate: 80 ml/min). All samples were measured in cylinder-like corundum crucibles.

metal-exchanged zeolite SCR catalysts and moisture on the decomposition has to the best of our knowledge not sufficiently been investigated. A straightforward approach to study the urea thermolysis and hydrolysis is thermogravimetric analysis (TGA), where mass loss is continuously measured with temperature. In Fig. 1 the results of the TGA measurements of the urea decomposition in dry N_2 are depicted. Additionally, the simultaneously measured differential thermoanalysis (DTA) spectrum as well as the concentration of evolved gases detected online by GC/MS are shown.

The sharp endothermic DTA peak at 133 °C corresponds to the melting point of urea. Immediately after melting the sample starts losing mass. DTA signals peaking in the range of 150–250 °C obviously reflect different urea decomposition reactions. At about 270 °C a plateau with nearly no additional mass loss is reached. Remarkably, at this temperature only 50% of the original urea mass is decomposed to gaseous products, whereas the other 50% remain as white powder in the crucible. By means of GC/MS we could quantitatively detect the four gases CO_2 , NH_3 , $HNCO$, and H_2O as products in the course of the decomposition. Fig. 1 shows that the mass loss is accompanied by the evolution of huge amounts of NH_3 peaking at 200 °C as well as by an endothermic DTA signal. According to reaction (1) urea first thermolyses to NH_3 and $HNCO$ in an endothermic reaction ($\Delta_R H = 185.5$ kJ/mol) explaining both the evolution of NH_3 and the DTA peak in Fig. 1. However, only a minor amount of $HNCO$ was detected between 210 and 270 °C. The weak evolution of CO_2 at 200 °C can be explained by the hydrolysis of

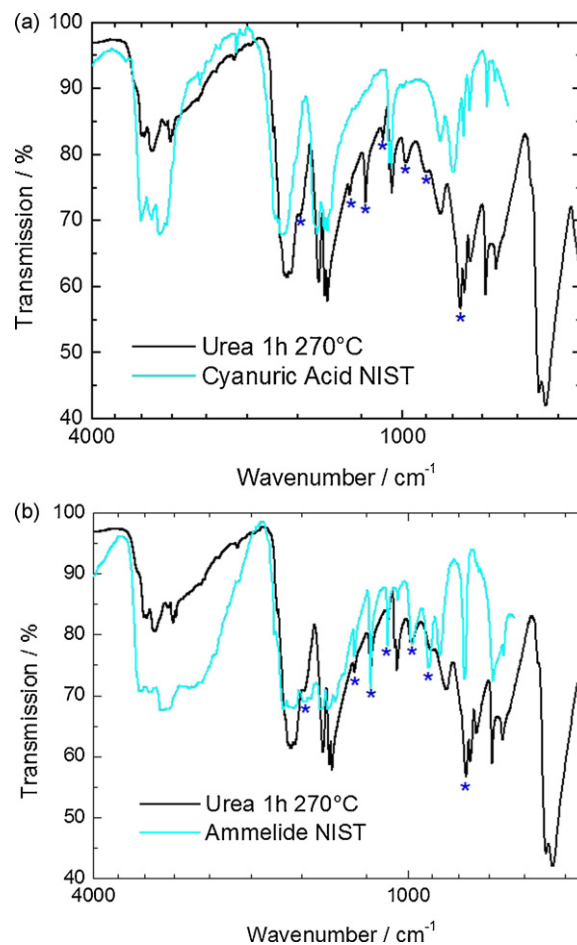


Fig. 2. ATR-FTIR spectra of urea decomposed for 1 h at 270 °C in dry N_2 and comparison with cyanuric acid (a) and ammelide (b) reference spectra. Peaks marked with asterisks indicate bands that are exclusively characteristic for ammelide.

$HNCO$ with trace amounts of water in the original sample to NH_3 and CO_2 after reaction (2).

In order to characterize the solid intermediates at 270 °C, a urea sample was isothermally treated in dry N_2 for 1 h at 270 °C. The solid residues were analyzed by means of ATR-FTIR. The obtained FTIR spectrum is depicted in Fig. 2. As mentioned before, several authors reported that CyA is an intermediate product of the pyrolysis of urea [14,16,20,21,23]. Indeed, comparing the FTIR spectrum of our sample with a CyA reference spectrum gives a very good match (Fig. 2a).

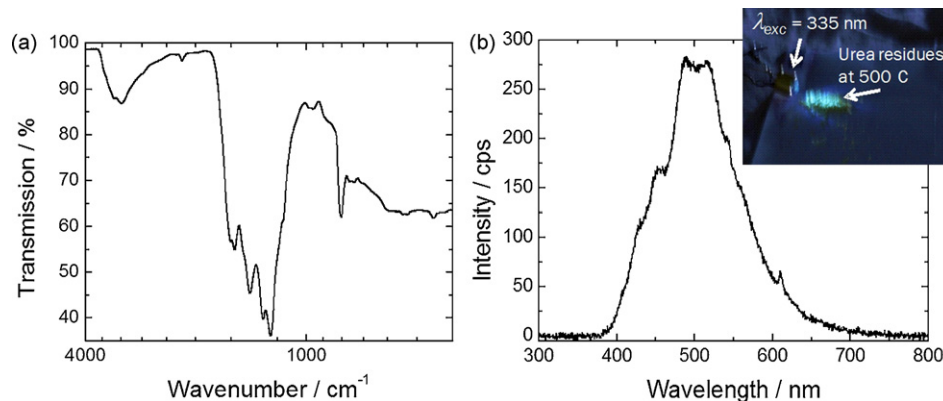


Fig. 3. ATR-FTIR (a) and luminescence spectrum (b, excitation with 337 nm) of urea decomposed for 1 h at 500 °C in dry N_2 . Inset: Image of 500 °C urea residues irradiated with a 335 nm UV-LED.

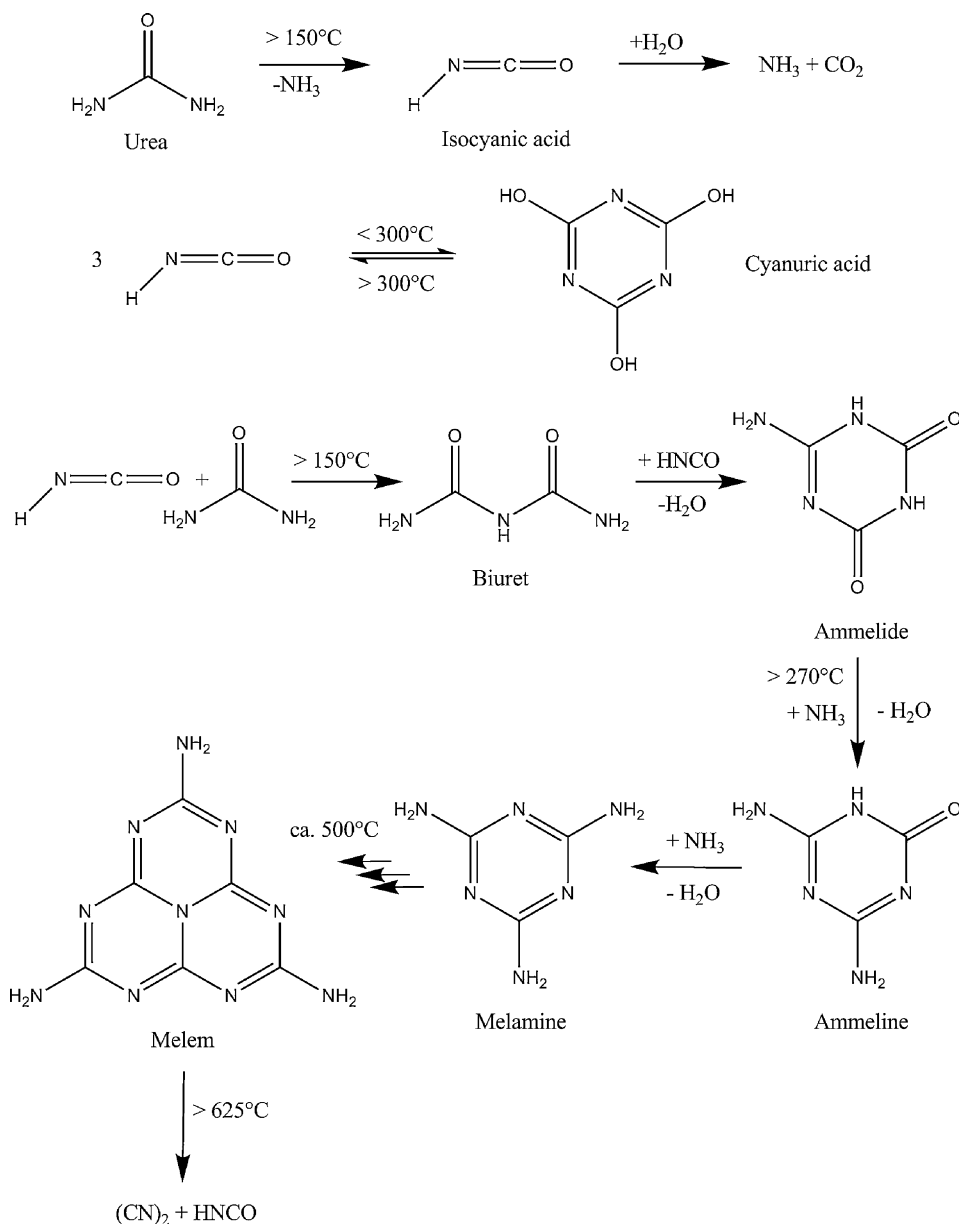


Fig. 4. Schematic of all major reactions, intermediate and final products for the pyrolysis and hydrolysis of neat urea in the temperature range between 20 and 750 °C.

Bands in the fingerprint region at 660, 691, 741, 760, and 844 cm^{-1} , the in-plane ring stretch at 1050 cm^{-1} , ring vibrations at 1454, 1414, and 1398 cm^{-1} , the characteristic C=O stretch at 1676 cm^{-1} as well as bands in the O–H region between 2800 and 3200 cm^{-1} all show an excellent overlap with the CyA reference. Though peaks at 773, 904, 986, 1092, 1180, 1266, and 1578 cm^{-1} cannot be assigned to the CyA spectrum, they match perfectly with the reference spectrum of ammelide as shown in Fig. 2b. FTIR spectra of alternative possible decomposition products such as biuret, ammeline or melamine do not overlap well with the spectrum of decomposed urea. Consequently, the pyrolysis of urea at 270 °C yields CyA and ammelide as main solid products. CyA can be formed either by the reaction between biuret and HNCO, biuret and urea or by direct trimerization of HNCO in a strongly exothermic reaction ($\Delta_R H = -336 \text{ kJ/mol}$). Ammelide is a product of the reaction between HNCO and biuret. Therefore, the dip at about 240 °C in the DTA spectrum (Fig. 1) can be interpreted in terms of an overlap between the exothermic signal of CyA and ammelide formation and the endothermic bands of the thermolysis of urea, respectively.

Between 300 and 370 °C a large mass loss can be observed in the TGA spectrum (Fig. 1) accompanied by a sharp endothermic DTA signal peaking at 370 °C and the evolution of large amounts of HNCO. This can be explained by the thermolysis of CyA, which decomposes above 300 °C in an endothermic reaction ($\Delta_R H = 336 \text{ kJ/mol}$) to HNCO. Eventually, at 500 °C about 5% of the original mass remained as yellowish solid residues. In the appropriate FTIR spectrum of the 500 °C residue signals at 3345 and 3200 cm^{-1} in the NH stretching mode range, at 1605, 1565, 1420, 1310, and 1250 cm^{-1} , which is the characteristic range for CN heterocycles, and the triazine ring bending mode at 800 cm^{-1} can be identified (Fig. 3a).

Comparison with literature spectra of the heptazines melem and melon [26–28] gives an excellent match between the characteristic bands. Another method to distinguish between triazines (such as ammeline, melamine) and heptazines (such as melem, melon) is photoluminescence spectroscopy. While heptazines are characterized by an intense green luminescence with excitation in the UV, triazines do not show an appreciable visible emission

[27,29]. Fig. 3b indicates that indeed the 500 °C urea pyrolysis residues exhibit an intense green luminescence peaking at 500 nm with 337 nm excitation, which is further evidence that at 500 °C heptazines such as melem are formed and not triazines such as melamine. Melem is formed by the polymerization of melamine, whereas melon is the polymerized product of melem.

In addition, the decomposition of the heptazine residues above 500 °C was investigated. The TGA-GC/MS experiment showed clearly that above 625 °C the solid intermediates start decomposing to cyanogen (CN)₂ (data not shown). Minor amounts of HNCO could be detected, too. Eventually, at 750 °C nearly 100% of the original urea mass is decomposed. A summary of the major reactions during the decomposition of neat urea is given in Fig. 4.

3.2. Pyrolysis of urea over zeolites

For a better understanding of the urea decomposition processes on the surface of SCR catalysts, it is necessary to study the influence of the zeolites on the urea decomposition. Fang et al. investigated recently the influence of vanadia SCR catalysts on the urea decomposition [14]. They observed that by decomposing urea in a mixture with this catalyst the formation of possibly poisoning solid by-products such as CyA could be prevented or at least reduced. In order to identify the impact of zeolite catalysts, we prepared 1:1 mixtures of the zeolite and urea by mechanically mixing the components using mortar and pestle. Additionally, we prepared an aqueous solution containing 32.5% urea by weight and impregnated zeolite powders in such a way, that the final zeolite:urea mass ratio yielded 1:1. Subsequently, samples were dried at room temperature for 72 h. Fig. 5a depicts the TGA/DTA curves for the decomposition of urea mechanically mixed with Fe-Beta.

It is unambiguous that Fe-Beta alters significantly the urea decomposition process. First, both the urea thermolysis to NH₃ and the decomposition of solid intermediate products is shifted to lower temperatures (160 and 290 °C instead of 200 and 370 °C, respectively). Furthermore, the formation of solid residues in the 200–300 °C range is decreased tremendously. The results of the GC/MS evolved gas analysis depicted in Fig. 5a also show that at 170 °C more NH₃ and CO₂ are formed than during the decomposition of pure urea. Additionally, a CO₂ peak appears at 300 °C, too, which was not observed in this temperature range for the decomposition of pure urea. As mentioned in the introduction zeolites can catalyze the hydrolysis to HNCO via reaction (2). This explains the generation of larger amounts of NH₃ and CO₂ at 120–220 °C and the evolution of CO₂ at about 300 °C. The missing NH₃ evolution in the latter temperature range can be explained by the consumption of ammonia to form solid products such as ammeline and melamine generated by the reaction of cyanuric acid or ammeline with NH₃ (Fig. 4), the adsorption of significant amounts of NH₃ by the zeolite, and/or the lower NH₃ sensitivity as compared to CO₂ of our GC/MS setup (stainless steel lines can adsorb NH₃). The adsorption of significant amounts of product gases even at higher temperatures is indicated by the constant non-zero CO₂ GC/MS signal at 350–500 °C and the appropriate nearly constant mass loss.

Fig. 5b shows that the evolved gaseous products reflect very well the observed mass loss in the TGA experiment. Here, the measured mass loss is compared with the temperature-dependent summation of total gas mass as detected by GC/MS evolved gas analysis giving a very good agreement between the two measurements.

The overall trend of the zeolite-based shift of the urea pyrolysis to lower temperatures was also found for mixtures of urea with zeolites H-Y, Cu-Y, H-Beta, and Na-Beta (Fig. 6). The effect of hydrothermally aged (h.a.) zeolites on the pyrolysis of urea is depicted in Fig. 6, too.

For this purpose Fe-Beta powder was aged for 20 h in 10% steam, 10% O₂, and 80% N₂ at 750 °C and subsequently mixed with urea.

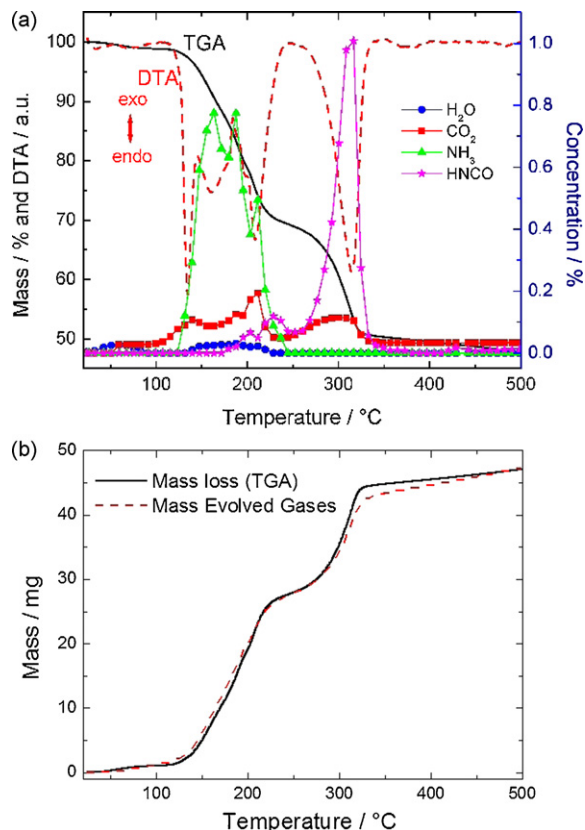


Fig. 5. (a) TGA, DTA graphs and quantitative results of the GC/MS evolved gas analysis of the decomposition of urea/Fe-Beta 1:1 mixture in dry N₂ (initial weight: 90 mg; heating rate: 2 K/min; flow rate: 80 ml/min). (b) Comparison of the mass loss as measured by TGA with the temperature-dependent summation of the mass of gaseous products as detected by GC/MS evolved gas analysis. All samples were measured in cylinder-like corundum crucibles.

Obviously, hydrothermal aging decreases the activity to catalyze the urea decomposition since the formation of larger amounts of urea decomposition by-products in the 250–325 °C range was observed. Interestingly, the corresponding TGA curve matches very

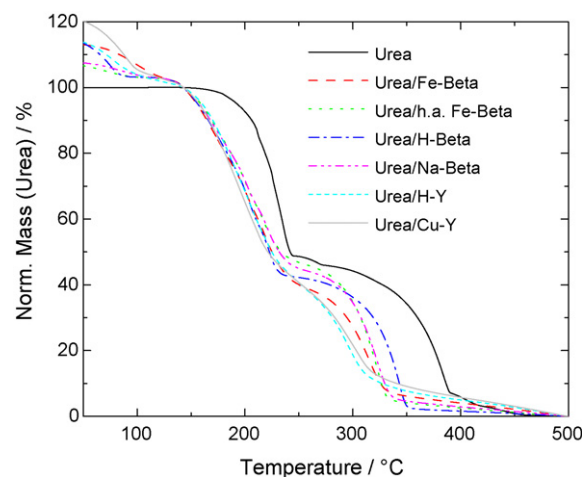


Fig. 6. TGA graphs of the decomposition of neat urea (initial weight: 60 mg) and of different urea/zeolite 1:1 mixtures (initial weight: 80 mg) in dry N₂ (heating rate: 2 K/min; flow rate: 80 ml/min). For better comparison spectra were normalized by defining the masses at 150 °C as 100 wt.% and at 500 °C as 0 wt.%. h.a. Fe-Beta refers to Fe-Beta powder hydrothermally aged for 20 h at 750 °C in 10% steam, 10% O₂ and 80% N₂ at GHSV = 30,000 cm³ g⁻¹ h⁻¹. All samples were measured in cylinder-like corundum crucibles.

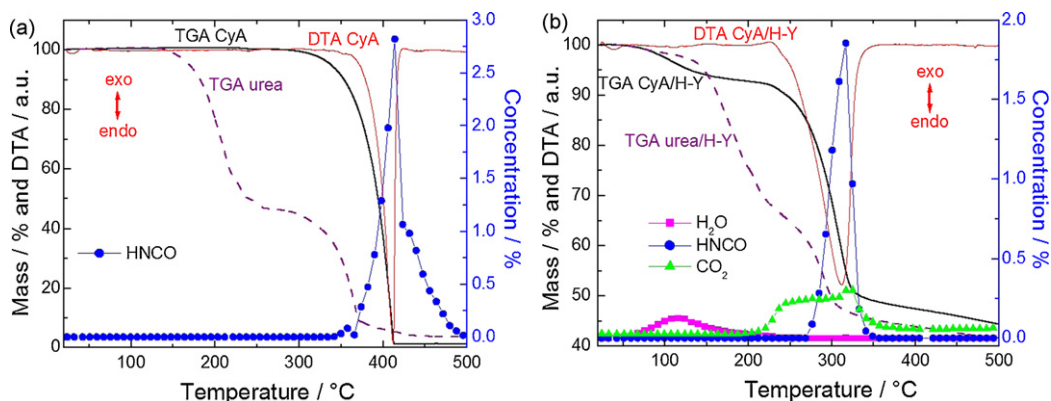


Fig. 7. TGA, DTA graphs and quantitative results of the GC/MS evolved gas analysis of the decomposition of neat cyanuric acid (a, initial weight: 75 mg) and of a cyanuric acid/H-Y 1:1 mixture (b, initial weight: 112 mg) in dry N₂ (heating rate: 2 K/min; purge gas: dry N₂, 80 ml/min). For comparison, TGA curves of neat urea and of a urea/H-Y 1:1 mixture, respectively, are shown as well. All samples were measured in cylinder-like corundum crucibles.

well with the appropriate graph of urea/Na-Beta mixtures that do not contain Fe ions. Moreover, our studies indicate that the positive catalytic effect in preventing the formation of solid intermediate products decreases in the order H-Y, Cu-Y > Fe-Beta > Na-Beta, h.a. Fe-Beta > H-Beta. Roughly, the catalytic activity correlates with the acidity of the zeolites. Measuring the amount of adsorbed NH₃ at 150 °C by means of TGA of the appropriate zeolite powders, which can be regarded as an indicator for the acidic strength of the catalysts, gives a similar trend: Cu-Y (4.3 wt.% NH₃) > H-Y (3.7 wt.%) > Fe-Beta (2.35 wt.%) > Na-Beta (1.93 wt.%) > h.a. Fe-Beta (0.69 wt.%) > H-Beta (0.56 wt.%). Thus, we speculate that especially acidic sites such as Brønsted sites are the active species in the decomposition of urea, since these sites can bind very strongly N-containing species and are supposed to play a major role in the SCR reaction between NH₃ and NO or NO₂ also [3]. However, Fe-containing beta zeolites exhibit among beta zeolites the highest acidity as well as the highest activity towards the decomposition of urea. Hence an involvement of Fe sites, i.e. Lewis sites, in the urea pyrolysis cannot be excluded either. Additionally, we investigated urea/zeolite mixtures prepared by impregnating zeolite powders with aqueous 32.5 wt.% urea solution, but no differences between those and mechanically mixed samples regarding the urea decomposition process could be determined except the increased mass loss below 150 °C due to the evaporation of water.

Since the decomposition of solid intermediates in the range between 200 and 370 °C is significantly shifted to lower temperatures under the influence of zeolites, the question arises whether this is only due to the zeolite catalyzed hydrolysis of HNCO after reaction (2), thus inhibiting the formation of CyA due to the lower HNCO concentration, or whether zeolites can even catalyze the decomposition of CyA itself. Consequently, we studied the pyrolysis of neat CyA and of CyA/zeolite 1:1 mixtures, too. Fig. 7a shows that pure CyA is decomposed at about 410 °C as indicated by the evolution of HNCO and the strong endothermic DTA signal. No other gases such as NH₃ or CO₂ were observed as decomposition products. This behavior reflects nearly perfectly the TGA curve shape and product gas analysis of the second stage of urea decomposition above 300 °C, thus giving further evidence that CyA is a main urea pyrolysis solid intermediate product. However, above 410 °C only about 1.3% of the original CyA remains as solid residues as opposed to the 5% for the decomposition of pure urea. This finding indicates that the solid products of urea at 500 °C, which were identified as heptazines, are not formed in the same amount during the pyrolysis of CyA. Thus, it is very likely that precursors such as ammelide, ammeline and melamine, that are formed only during urea pyrolysis, are needed instead for the formation of heptazines. Interestingly, the addition of zeolites such as H-Y induces

a dramatic decrease of the decomposition temperature to 310 °C (Fig. 7b). Furthermore, besides HNCO, CO₂ can be identified as gaseous product indicating the partial hydrolysis of HNCO by traces of water present in the zeolite. These findings as well as the excellent match of this TGA curve with the second decomposition stage of urea in a mixture with zeolite H-Y confirms that zeolites can indeed catalyze the decomposition of CyA and that this reaction can perfectly explain the large reduction of solid urea decomposition residues at 200–470 °C in mixtures with zeolites. Similar results were also found for other zeolites such as Fe-Beta.

3.3. The influence of moisture

In this section, the influence of water on the urea decomposition will be discussed. Since diesel exhaust usually contains around 5% steam and since the hydrolysis of HNCO to NH₃ and CO₂ is a crucial step in the urea decomposition process, it is very important to investigate this issue thoroughly. Fig. 8 gives a comparison of the TGA curves of the decomposition of pure urea and urea-impregnated Fe-Beta mixtures (Urea/Fe-Beta mass ratio of 1:1) in dry N₂ and N₂ containing 5–6% steam, respectively.

The results indicate that in case of neat urea water has only an appreciable impact on the decomposition at higher temperatures (> 400 °C). Here, steam reduces significantly the formation of solid intermediates previously identified as heptazines, e.g. at

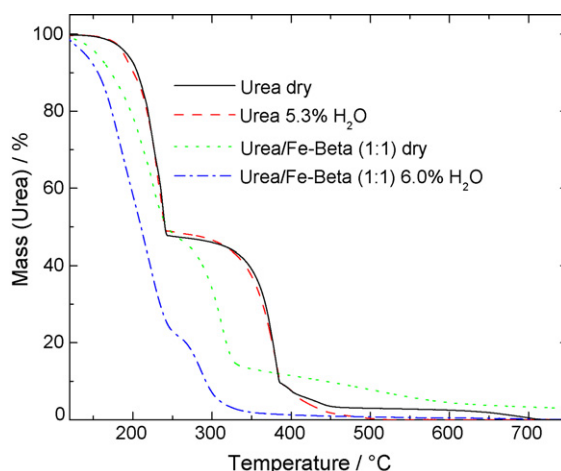


Fig. 8. TGA graphs of the decomposition of neat urea (initial weight: 50 mg) and of urea-impregnated Fe-Beta (1:1 mixtures; initial weight: 50 mg) in both dry and water-containing N₂ (heating rate: 5 K/min; flow rate: 200 ml/min). All samples were measured in cylinder-like corundum crucibles.

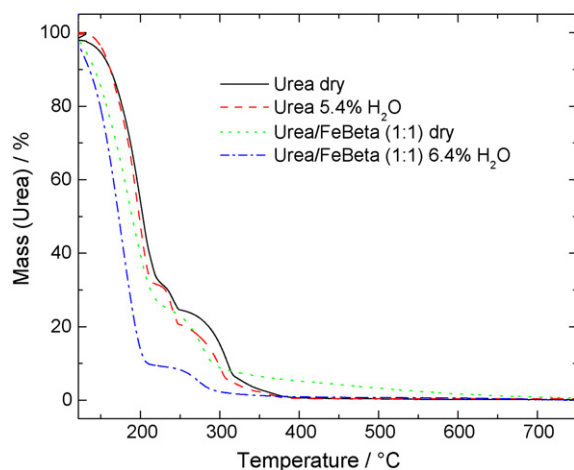


Fig. 9. TGA graphs of the decomposition of neat urea (initial weight: 45 mg) and of urea-impregnated Fe-Beta (1:1 mixtures; initial weight: 50 mg) in both dry and water-containing N_2 (heating rate: 5 K/min; flow rate: 200 ml/min). All samples were measured in flat plate-like corundum crucibles.

500 °C the residues are reduced from 3.0 ± 0.6 to $0.3 \pm 0.1\%$ of the original urea mass. As already reported in the preceding section zeolites such as Fe-Beta catalyze the pyrolysis of urea and cyanuric acid, respectively. As also shown in Fig. 8 the decomposition of urea-impregnated Fe-Beta in a steam-containing atmosphere is tremendously altered. First, the pyrolysis of urea starts already at the melting point of 133 °C, and second, the formation of solid intermediates is significantly inhibited, e.g. at 250 °C the amount of solid residues was reduced from 48 to 23% of the original mass. Furthermore, at temperatures above 300 °C residual molecules that adsorb strongly on the zeolite even at higher temperatures such as CO_2 , NH_3 and $HNCO$ are obviously removed efficiently under the influence of water. Consequently, at 500 °C only 0.7 wt.% instead of 7.8 wt.% urea residues are left on the catalyst. Finally, at 750 °C no solid decomposition compounds or adsorbents remain on the catalyst, whereas in dry atmospheres still 2.9 wt.% are left. Moreover, the results of the GC/MS evolved gas analysis indicate that any formed $HNCO$ is immediately hydrolyzed to NH_3 and CO_2 , since we could not detect any gas phase $HNCO$, but huge amounts of CO_2 instead (data not shown).

While for all previous TGA experiments a cylinder-like crucible with a height of about 1.3 cm and an inner diameter of 0.7 cm was used as sample holder, Fig. 9 depicts TGA results of the decomposition of neat urea and urea-impregnated Fe-Beta in a flat plate-like crucible having a diameter of about 1.7 cm. As a result, the total amount of formed solid by-products is reduced for all samples in both dry and wet atmospheres over the entire temperature range. This can be interpreted in terms of a significantly enlarged sample surface that is directly exposed to the purge gases. Moreover, the plate-like crucible geometry enables the quick removal of intermediately formed product gases, thus avoiding high local concentrations of $HNCO$, whereas in the cylinder-like crucibles diffusion limitations might have hindered the emission of $HNCO$ below 300 °C. Consequently, due to the increased mass transfer the formation of solid polymeric $HNCO$ -derived products such as CyA is tremendously diminished. Since the flow conditions in a “real” flow-through catalyst system mounted in a diesel exhaust pipe are supposed to be more similar to the conditions in the plate-like crucible, the urea decomposition scenarios shown in Fig. 9 should be the most realistic ones. However, qualitative measures such as the kind of gaseous and solid products formed during thermolysis and hydrolysis were not changed by the crucible geometry, i.e. the previous interpretation of urea decomposition mechanisms is not influenced.

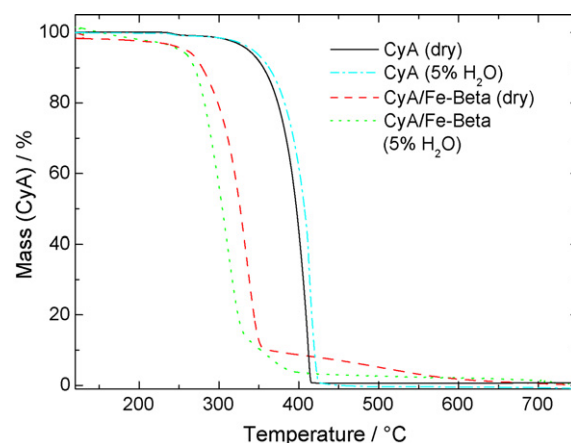


Fig. 10. TGA graphs of the decomposition of neat cyanuric acid (initial weight: 40 mg) and of cyanuric acid/Fe-Beta 1:1 mixtures (initial weight: 40 mg) in both dry and water-containing N_2 (heating rate: 5 K/min; flow rate: 200 ml/min). All samples were measured in cylinder-like corundum crucibles.

Finally, we studied the influence of moisture on the decomposition of CyA. Fig. 10 depicts the decomposition in dry N_2 of pure CyA and of a CyA/Fe-Beta 1:1 mixture as well as the decomposition of both neat CyA and a CyA/Fe-Beta 1:1 mixture (prepared by mechanically mixing the constituents) with 5% steam in N_2 as measured by TGA (all samples measured in a cylinder-like crucible).

As a result, the pyrolysis temperature remains nearly the same for pure CyA, but is shifted for CyA/Fe-Beta to a lower temperature under the influence of water. For example, while without moisture 50 wt.% of CyA in a mixture with Fe-Beta are decomposed at 326 °C, this value is shifted to 304 °C in a water-containing atmosphere. This effect can be explained by the immediate hydrolysis of the thermolysis product $HNCO$ to NH_3 and CO_2 after reaction (2) shifting the decomposition equilibrium towards the products. Another effect of moisture is the increased desorption of the decomposition products $HNCO$, NH_3 and CO_2 above 400 °C due to competitive H_2O adsorption, which was already observed for the decomposition of urea mixed with Fe-Beta in wet atmospheres (Fig. 8).

In order to derive apparent kinetic data for the decomposition of neat urea as well as of urea in mixtures with Fe-Beta catalysts, samples were isothermally treated for 2 h at 160, 260, and 300 °C, respectively, and the mass loss was measured by means of TGA. The three specific temperatures were chosen since they reflect the three main stages observed during the decomposition of neat urea: (1) the pyrolysis of urea to $HNCO$ and NH_3 (and the formation of biuret and triuret) accompanied by a significant mass loss between 150 and 250 °C, (2) the formation of CyA reflected by the mass plateau between 270 and 300 °C, and (3) the pyrolysis of CyA to $HNCO$ above 300 °C which was tremendously shifted to lower temperatures under the influence of zeolites and moisture.

Assuming only first-order reactions the weight loss can be represented by an exponential decay: $m_i - m_r = (m_0 - m_r) \times \exp(-kt)$, with m_i and m_r being the actual mass and the mass of residues not decomposable at the measured temperature, respectively, m_0 being the initial mass at this temperature, k being the apparent rate constant, and t the time. Thus, plotting $\ln(m_i - m_r)$ versus t gives a linear function with the slope $-k$. For certain samples and at specific temperatures multiple decomposition regimes were identified, i.e. a rapid mass loss was followed by one or even two slower mass loss regimes. In these cases the multiple linear ranges of $\ln(m_i - m_r)$ (that could be easily separated due to slopes that differed by at least one order of magnitude) were plotted versus t and each range was fit by linear regression, thus giving multiple slopes and apparent rate constants k , respectively, at one temperature. These different rate constants were interpreted in terms of different consecutive

Table 1

Apparent kinetic rate constants k [min^{-1}] for the decomposition of neat urea and of urea-impregnated Fe-Beta (1:1 mixtures) in both dry and wet atmospheres at different temperatures as measured by means of TGA. All samples were measured in cylinder-like corundum crucibles.

Sample	k at 160 °C	k at 260 °C	k at 300 °C
Neat urea (dry N_2)	3.67×10^{-3}	9.72×10^{-4}	9.40×10^{-3}
Urea/Fe-Beta (dry N_2)	8.12×10^{-3} 8.25×10^{-4}	1.41×10^{-3} 6.28×10^{-4}	8.17×10^{-5}
Urea/Fe-Beta (6.5% H_2O)	2.18×10^{-2} 4.25×10^{-3} 2.4×10^{-4}	4.74×10^{-5}	3.80×10^{-5}

or parallel reactions. The results of this kinetic analysis are summarized in Table 1.

While the first pyrolysis step of neat urea at 160 °C in dry N_2 with a rate constant of $3.7 \times 10^{-3} \text{ min}^{-1}$ is quite fast, the subsequent decomposition of the intermediate products at 260 °C is rather slow. Only at 300 °C a significant mass loss due to CyA pyrolysis is reflected by the relatively large rate constant of $9.4 \times 10^{-3} \text{ min}^{-1}$. As already discussed in the previous paragraphs, Fe-Beta accelerates both the pyrolysis of urea and CyA, which is reflected by the increased rate constants at 160 and 260 °C. The rate at 160 °C is increased by a factor of 2.2, whereas the CyA decomposition rate at 260 °C is increased by 1.5. However, at 160 °C a second rate constant with a value of $8.3 \times 10^{-4} \text{ min}^{-1}$ could be derived, which could be assigned to the beginning decomposition of CyA, but also to the hydrolysis of HNCO. Obviously, at 300 °C the decomposition of residual CyA is negligible and its small rate constant of $8.2 \times 10^{-5} \text{ min}^{-1}$ is most probably associated with the formation or decomposition of other intermediate products such as ammelide, ammeline, melamine or melon, or the desorption of gaseous products such as CO_2 , NH_3 , and HNCO. The peculiar influence of moisture on the decomposition of urea can be unambiguously seen in the appearance of three different rather large rate constants at 160 °C for urea/Fe-Beta mixtures, whereas at higher temperatures only very small rate constants could be identified. This can be explained in terms of a tremendous shift of nearly all reactions that play a major role in the decomposition of urea to lower temperatures. The pyrolysis of urea to HNCO and NH_3 is most likely reflected by the rate constant of $2.2 \times 10^{-2} \text{ min}^{-1}$, which would correspond to an acceleration of this reaction by factors of 6 and 2.7, respectively, if compared to neat urea and urea/Fe-Beta mixtures in dry atmospheres, respectively. The other two rate constants can be associated most likely with the formation and decomposition of other intermediate products and/or the hydrolysis of HNCO to NH_3 and CO_2 , and the subsequent desorption of these gases from the catalyst surface.

4. Conclusions

By mixing various zeolite catalysts (H-Y, Cu-Y, H-Beta, Na-Beta, Fe-Beta) with urea via impregnation or mechanical mixing the impact of zeolites on the pyrolysis and hydrolysis of urea in the temperature range between 20 and 750 °C was investigated. Thus, the decomposition of urea deposits on SCR catalysts formed during urea injection into the diesel exhaust at low exhaust temperatures could be simulated. As for the decomposition of neat urea, TGA/DTA and online GC/MS evolved gas analysis indicate that urea first decomposes to HNCO and NH_3 . ATR-FTIR spectroscopy investigations of the solid intermediate products at 270 °C show that most of the HNCO reacts to CyA and ammelide. At 500 °C most of the solid residues are decomposed to gaseous HNCO, whereas a small amount of solid heptazines such as melem and melon, characterized by a green photoluminescence, is also generated. These

species decompose to gaseous components such as isocyanic acid (HNCO) and cyanogen ($(\text{CN})_2$) only at temperatures above 625 °C. Furthermore, our experiments clearly show that the investigated zeolites significantly accelerate the urea decomposition process. The studied catalysts shift both the pyrolysis of urea to NH_3 and HNCO and the decomposition of the intermediate product CyA to lower temperatures. Whereas the presence of steam in the purge gas has only little influence on the decomposition of neat urea, it prevents dramatically the formation of solid residues and shifts the urea decomposition in general to lower temperatures for urea/zeolite mixtures. This effect is due to the hydrolysis of HNCO to NH_3 and CO_2 catalyzed by the zeolites, thus avoiding large local concentrations of HNCO and consequently the formation of solid HNCO-derived by-products such as CyA. As a conclusion, even though zeolites, moisture, and optimized mass transfer conditions can significantly reduce the amount of solid by-products, at temperatures below 300 °C still appreciable amounts of solid residues are stable on the catalyst, and thus could harm the SCR performance of zeolites, if the exhaust temperature does not temporarily exceed this temperature limit in order to initiate their decomposition.

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References

- [1] R. Heck, R. Farrauto, Appl. Catal. A 221 (1–2) (2001) 443–457.
- [2] R.M. Heck, R.J. Farrauto, Catalytic Air Pollution Control: Commercial Technology, 3rd edition, Wiley and Sons, Hoboken, NJ, 2002, 2009.
- [3] S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff, Catal. Rev. 50 (4) (2008) 492–531.
- [4] P. Gabrielsson, Top. Catal. 28 (1–4) (2004) 177–184.
- [5] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B 18 (1–2) (1998) 1–36.
- [6] I. Chorkendorff, J.W. Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, Wiley-VCH, 2007.
- [7] W. Held, A. König, T. Richter, Catalytic NO_x Reduction in Net Oxidizing Exhaust Gas, SAE Technical Paper (1990) 900496.
- [8] M. Köbel, M. Elsener, M. Kleemann, Catal. Today 59 (3–4) (2000) 335–345.
- [9] H. Sjoval, L. Olsson, E. Fridell, R.J. Blint, Appl. Catal. B 64 (3–4) (2006) 180–188.
- [10] M. Devadas, O. Kröcher, M. Elsener, A. Wokaun, G. Mitrikas, N. Soger, M. Pfeifer, Y. Demel, L. Mussmann, Catal. Today 119 (1–4) (2007) 137–144.
- [11] M. Iwasaki, K. Yamazaki, K. Banno, H. Shinjoh, J. Catal. 260 (2) (2008) 205–216.
- [12] A. Frey, S. Mert, J. Due-Hansen, R. Fehrmann, C. Christensen, Catal. Lett. 130 (2009) 1–8.
- [13] M. Köbel, E.A. Strutz, Ind. Eng. Chem. Res. 42 (10) (2003) 2093–2100.
- [14] H.L. Fang, H.F.M. DaCosta, Appl. Catal. B 46 (1) (2003) 17–34.
- [15] S. Yim, S. Kim, J. Baik, I. Nam, Y. Mok, J. Lee, B. Cho, S. Oh, Ind. Eng. Chem. Res. 43 (16) (2004) 4856–4863.
- [16] A. Lundström, B. Andersson, L. Olsson, Chem. Eng. J. 150 (2009) 544–550.
- [17] G. Piazzesi, M. Devadas, O. Kröcher, M. Elsener, A. Wokaun, Catal. Commun. 7 (8) (2006) 600–603.
- [18] G. Piazzesi, D. Nicosia, M. Devadas, O. Kröcher, M. Elsener, A. Wokaun, Catal. Lett. 115 (1–2) (2007) 33–39.
- [19] I. Czekaj, O. Kröcher, G. Piazzesi, J. Mol. Catal. A 280 (1–2) (2008) 68–80.
- [20] P. Schaber, J. Colson, S. Higgins, D. Thielen, B. Anspach, J. Brauer, Thermochim. Acta 424 (1–2) (2004) 131–142.
- [21] L. Stradella, M. Argentero, Thermochim. Acta 219 (1993) 315–323.
- [22] E. Seker, N. Yasyerli, E. Gulari, C. Lambert, R.H. Hammerle, Appl. Catal. B 37 (2002) 27–35.
- [23] L. Xu, W. Watkins, R. Snow, G. Graham, R. McCabe, C. Lambert, R.O. Carter III, SAE (2007), 2007–01-1582.
- [24] Y. Cheng, J. Hoard, C. Lambert, J.H. Kwak, C.H.F. Peden, Catal. Today 136 (1–2) (2008) 34–39.
- [25] M. Eichelbaum, A.B. Siemer, R.J. Farrauto, M.J. Castaldi, Appl. Catal. B 97 (2010) 98–107.
- [26] A.L. Finkelshtein, N.V. Spiridonova, Russ. Chem. Rev. 33 (7) (1964) 400–405.
- [27] J.R. Holst, E.G. Gillan, J. Am. Chem. Soc. 130 (23) (2008) 7373–7379.
- [28] M.J. Bojds, J.O. Müller, M. Antonietti, A. Thomas, Chem. Eur. J. 14 (27) (2008) 8177–8182.
- [29] D.R. Miller, D.C. Swenson, E.G. Gillan, J. Am. Chem. Soc. 126 (17) (2004) 5372–5373.